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Development of narrow band emitting phosphors for backlighting displays and solid state lighting using a clean and green energy technology

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ABSTRACT

The development of phosphors with efficient narrow-band and tunable emission in the entire visible region is an important issue in solid-state-lighting and backlighting displays related to energy saving and environmentally friendly technology. To modify the emission color and to maximize the luminescence characteristics, oxides and nitrides as well as various cation substitutions are often used. Nonetheless, the existing mechanisms do not satisfactorily describe the above characteristics. The factors which define the luminescence features are the centroid shift, Stokes shift, crystal field splitting, and bandwidth. This study comprehensively describes these characteristics, along with the role of cation substitutions in UCr_4C_4 type compounds. To efficiently control the factors that govern the luminescence characteristics, several structural strategies are proposed, including (1) chemical composition and crystal structure modifications, (2) alteration of an appropriate activator crystallog graphic site, and (3) control of the crystalline phase transition. White LEDs manufacturing and state-of-the-art applications, including wide color gamut display and full-spectrum solid-state lighting, along with near-infrared technology are thoroughly discussed. Challenges and potential prospects are also suggested. The ultimate aim of this paper is to contribute to the effort for producing novel materials which will be suitable for the next-generation of phosphors that can be used in various emerging energy applications.

1. Introduction

The combination of a blue LED chip with yellow emitting YAG: Ce^{3+} phosphors is successfully utilized in the majority of the devices used to produce white light nowadays; yet, the light obtained from this combination does not satisfy the requirements of home and office lighting due to the absence of the red color component. In addition, YAG: Ce^{3+} emits a broad emission band that is not suitable for liquid crystal displays (LCDs) backlight. To fabricate white-LEDs with a high color rendering index (CRI) and low correlated color temperature (CCT),

highly efficient red-emitting, green-emitting, and blue-emitting phosphors that can be effectively excited by ultraviolet (UV), near-UV, and blue LEDs, must be produced. More specifically, the narrow-band red-emitting phosphors will solve the problem of the red color deficiency in the commercially available YAG: Ce^{3+} phosphors used for general illumination, while the combination of narrow-band red, green, and blue (RGB) phosphors will allow the fabrication of high-quality displays.

Phosphors with narrow-band emission in the green and red spectral region are continuously studied in order to improve the maximum color gamut, the color quality (high CRI value > 90), and the visual luminous

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efficacy for generating an efficient white light source. Phosphors converted white light-emitting diodes (pc-LEDs) have various applications, such as highly efficient mercury-free emission, long operation lifetime, fast switching time and dimming, etc. [1–3] There are various applications of white LEDs converted phosphors. Among them, we distinguish the backlight for liquid crystal displays (LCDs), whose color gamut is strongly affected by the chromaticity color coordinates of the red/-green/blue (RGB) emissions [4]. The development of phosphors with a suitable peak position, high photoluminescence quantum efficiency (near unity, i.e. 100%), excellent chemical and thermal stability, and narrow-band emission is, therefore, an essential task for satisfying the requirements of various applications.

To produce an enhanced saturated color, enormous color gamut, and minimum correlated color temperature, green and red-emitting phosphors are highly needed, which can be used in applications including backlighting for LCDs and general lighting lamps, etc. The green and red color components of Ba₂SiO₄:Eu²⁺, Sr₂Si₅N₈:Eu²⁺, and CaAlSiN₃:Eu²⁺ phosphors are very popular in recent years and are commercially available nowadays [1,4–8]. Their feature are the relatively wider emission, the great color refractive index, the top luminous efficacy, and the absence of narrow-band emission. Green and red sharp line emission can be a result of lanthanides f – f and d – d transition [9–13]. However, the absorption transition of these ions is forbidden in UV and blue light excitations [10,13,14].

In LCDs, the discovery and production of highly efficient narrowband emitting phosphors that can produce efficient and clear image with high color saturation is a great challenge. The efficient production of narrow band emitting materials will open a huge market. In other words, the lack of such novel narrow-band emitters is a significant obstacle for the development of LCDs backlighting.

Several rare-earths (RE^{3+}/RE^{2+}) doped phosphors are narrow-band emitters, such as β -SiAlON: Eu²⁺, SrGa₂S₄: Eu²⁺. Quantum dots (QDs), such as CdSe/ZnS, and perovskite CsPbBr₃, CsPbI₃ QDs have also been investigated. Nevertheless, the Cd-based QDs are toxic and the sulfide phosphors are unstable, which leads to a rapid degradation of their initial power [15–17]. In the overall achievable color gamut of the LCDs, the narrowest green-emitting phosphors (β -SiAlON: Eu²⁺) that are commercially available also have limitations. Perovskite QDs, such as CH₃NH₃PbBr₃ and CH₃NH₃PbI₃, are an emerging class of high-intensity narrow-band green and red emission materials with a high potential for a wide color gamut that is promising for backlight display applications, due to their high PLOYs (~90%) and the narrow-band emission in the FWHM that is in the range of $\sim 20-25$ nm [18]. However, CH₃NH₃PbX₃ decomposes to PbX₂ and volatile CH₃NH₃X due to the environment's stress, resulting in PLQYs loss. In addition, the presence of the environmentally unfriendly Pb²⁺ and the unstable PLQYs strongly influence negatively the commercial use of these materials [14,18]. Therefore, the production of new inorganic phosphors with narrow-band green and red emission is urgently needed for the commercialization of solid-state lighting.

Since the US 9,546,319 patent, which was filed by PHILIPS in 2013, the development of UCr₄C₄ type compounds with the synthesis of various narrow emitting phosphors has gained considerable interest [19]. The design of the UCr₄C₄ type structure of NaLi₃TiO₄, NaLi₃GeO₄, and NaLi₃SiO₄ was developed by Prof. Hoppe in 1986 [20]. In addition, the group of Prof. Schnick carried out a pioneer research on developing narrow band emitting nitride phosphors, and produced a narrow band emitting SrLiAl₃N₄:Eu²⁺ nitride phosphor with superior thermal stability [1]. That work on the narrow-band red-emitting Sr [LiAl₃N₄]: Eu²⁺ phosphors inspired novel strategies for developing the most modern narrow-band phosphors, which involve mineral-inspired prototype structure evolution and new phase preparation approaches.

Several new compositions with the UCr₄C₄ type structure, such as Sr [Mg₃SiN₄]: Eu^{2+} , Ba [Mg₂Ga₂N₄]: Eu^{2+} , CaLiAl₃N₄: Eu^{2+} , and Sr [Mg₂Al₂N₄]: Eu^{2+} , have been produced from the SrLiAl₃N₄: Eu^{2+} nitride phosphors [21–23]. In addition, Sr(LiAl₃)_{1-x} (SiMg₃)_xN₄: Eu^{2+} ,

CaBaLi₂Al₆N₈:Eu²⁺, SrLi(Al_{1-x}Ga_x)₃N₄:Eu²⁺, and Sr_{1-x}Ca_xLiAl₃N₄:Eu²⁺ nitride phosphors were synthesized and enriched the list of phosphors with characteristics, such as improved luminescence, various cation substitutions, and occurrence of solid solutions [24-27]. In our previous work, we investigated the enhancement of luminescence intensity with efficient substitution of the smaller Ca²⁺ for the larger Sr²⁺ in SrLiAl₃N₄: Eu^{2+} nitride phosphors [21]. A previous study showed that the development of compounds of UCr₄C₄ type structure nitrides was the primary focus for the preparation of narrow-band red emission, taking into account the demand related to the red color deficiency in YAG: Ce³⁺ phosphors converted LEDs [16]. These nitride phosphors emit highly efficient red color with excellent stability against moisture and temperature, due to the strong nephelauxetic effect, as a result of the presence of N³⁻ ions. These nitride phosphors are limited only to the orange and red color of the visible spectral region, which narrows their prospect for practical application in high color gamut LCD backlighting.

It was the group of Prof. Huppertz who introduced O^{2-} ions in UCr₄C₄ type nitride phosphors to successfully produce oxynitride phosphors, such as SrAl_{2-x}Li_{2+x}O₂₊₂xN_{2-2x}: Eu²⁺, Sr [Li₂Al₂O₂N₂]: Eu²⁺, and Na_{1-x}Eu_x [Li_{3-2x}Si_{1-x}Al_{3x}O_{4-4x}N_{4x}]: Eu²⁺, and achieved a shift of the emission spectrum towards shorter wavelengths of the visible spectral region. However, the tuning of the emission spectrum to shorter wavelength regions, such as blue or even green color emission, is still difficult to be achieved, despite the progress [28–30].

Based on the 2018/029,299 patent and the phosphors global summit meeting, OSRAM Opto Semiconductors tested a series of Eu²⁺ doped lithosilicate phosphors with UCr₄C₄ type structure, which provides an opportunity for the development of novel narrow-band shorter wavelength (blue, cyan, and green) emission phosphors [31]. The lithosilicate phosphors also display a cuboid and highly symmetric organized environment in the surrounding of the doped Eu²⁺ ions that result in a highly efficient narrow-band emission, similar to that of UCr₄C₄ type nitride and oxynitride phosphors. Many lithosilicate phosphors were developed by the group of Prof. Xia who also presented their potential for manufacturing white LEDs for practical general illumination and LCDs backlighting applications [32-36]. There are also interesting advancements in oxide phosphors in the UCr_4C_4 type compounds [37,38]. The lithosilicate phosphors offer more interesting possibilities for integrating Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺ ions in the crystallographic sites, compared to nitride and oxynitride phosphors of UCr₄C₄ type compounds. The variety in surrounding environments around the activated dopant in the host lattice is directly related to the different centroid shift, Stokes shift, and crystal field splitting, resulting in more complex structures with a high capability in the tuning ability of the emission color.

This paper reviews the latest development in the UCr₄C₄ type compounds in phosphors-converted LEDs used as a highly efficient white light source by fulfilling the deficiency of red color component and backlighting for displays. More specifically, the review focuses on the development of new narrow-band emitting UCr₄C₄ type compounds through the assessment of solid solutions and the formation of new phases through cations substitution strategies. An additional objective in the present review deals with the issue of photoluminescence tuning capability in the desired wavelength region to obtain adjustable photoluminescence emission color, which can be achieved by centroid shift alteration, Stokes shift, and crystal field splitting, as results of structural changes through chemical composition variation, crystal site engineering, and new phase formation. Finally, the research which has been conducted for developing white LEDs for general illumination, backlighting displays, and near-infrared technologies, is thoroughly discussed.

2. Influence of cation substitution on tuning of the 4f - 5 d spin allowed transition

2.1. Mechanism of the Eu^{2+}/Ce^{3+} luminescence tuning

The trivalent Ce³⁺ and the divalent Eu²⁺ ions, related to the 4f [6] \rightarrow 5d¹4f⁷ spin allowed transition, are the most frequently used activators in white LED phosphors due to their broadband emission. The characteristics of the surrounding host lattice, such as the host lattice symmetry and covalence character, bond lengths, and strength of the crystal field, strongly affect the emission spectrum.

Moreover, the emission color of the Ce^{3+}/Eu^{2+} doped phosphors can be effectively tuned in a wide range of visible light region from blue to red by selecting a suitable host or making some modifications in the host lattice. Nitride and oxynitride are ideal hosts for phosphors because of their outstanding characteristics, such as high chemical stability, tight chemical bonds, long-wavelength photoluminescence excitation, and emission. Furthermore, nitride and oxynitride, due to their rigid crystal structure, demonstrate superior thermal stability. Due to the strong covalent nature of N³⁻ in the host lattice of nitride and oxynitride phosphors [39–43], particularly large centroid shifts of the 5 d levels are expected to be induced by a strong nephelauxetic effect. In the light of the nephelauxetic effect, extensive research has been conducted on $\mathrm{Ce}^{3+}/\mathrm{Eu}^{2+}$ activated nitride and oxynitride phosphors, especially on Si-containing nitride and oxynitride phosphors, such as MSi₂O₂N₂:Eu²⁺ $(M = Ba^{2+}, Sr^{2+}, and Ca^{2+})$ [5,44,45], Ba(Si,Al)₅(O,N)₈:Eu²⁺ [46], and $Ba_3Si_6O_{12}N_2:Eu^{2+}$ phosphors [47].

In addition to the nephelauxetic effect induced by the polarization of host lattice anions, Stokes shift can also effectively allow $\text{Ce}^{3+}/\text{Eu}^{2+}$ emission color to be tuned and achieve high-quality white light, which is potentially related to host rigidity. The host lattice of phosphors with a more rigid crystal structure has a smaller Stokes shift and vice-versa. Therefore, the substitution scheme of $(Si^{4+}, N^{3-}) \rightarrow (Al^{3+}, O^{2-})$ is an effective way for allowing Ce^{3+}/Eu^{2+} photoluminescence to redshift to the desired wavelength. More specifically, the replacement of the small Si–N ($r_{Si} + r_N = 1.72$ Å) by the large Al–O ($r_{Al} + r_O = 1.77$ Å) induces an expansion in Ce³⁺/Eu²⁺ surrounding environment. Thus, the ground state equilibrium should be displaced, resulting in a large Stokes shift [5]. The luminescence center is strongly coupled with the rigidity of the host lattice, which plausibly has a high strength in sudden expansion. The Stokes shift and the shift of the emission spectrum towards longer wavelengths are influenced by this. However, high oxygen integration can induce a blue shift due to lower polarizability. Accordingly, parameters such as centroid shift, crystal field splitting, and Stokes shift can be adjusted by selecting the appropriate phosphors host lattice, which can effectively lead to the adjustment of the photoluminescence



$$\varepsilon_c = 1.79X10^{13} \sum_{k=1}^{N} \frac{\alpha_{sp}^i}{(R_i - 0.6\Delta R)^2}$$
(1)

where R_i indicates the gap in an undistorted host lattice between the activated Ce^{3+} and the anions i. The coordination of the activated Ce^{3+} and the factor $0.6\Delta R$ are used for the correction of host lattice relaxation around the activator (Ce^{3+}), and the sum indicates all anions (N). In addition, the α_{sp} shows the spectroscopic polarizability of the anions, which is an important factor contributing to the centroid shift with the effect of the associated motion and covalence between the activated Ce^{3+} and the anions along with other potential parameters.

2.1.2. Stokes shift

A large spectrum of photons of various wavelengths can be absorbed and released by inorganic materials. The highest peaks in the absorption and emission spectra attributed to the chemical composition of inorganic materials, are shown in Fig. 2 [54]. The difference between the highest absorption and emission peak is named Stokes shift. The effect of the Stokes shift on the induced redshift of the PL spectra can be interpreted using the Dorenbos study on phosphors (oxide, chloride, and bromide) [5,55].

The position of the peak point of photoluminescence excitation and emission can be typically determined by the crystal field splitting and the centroid shift. The band position of PLE and PL spectra is always effectively influenced by the Stokes shift related to host lattice rigidity. The centroid shift is proportional to the number of coordinates and spectroscopy polarizability in the host lattice of phosphors. It is also inversely proportional to the 6th power of bond length. The crystal field splitting of the phosphors host lattice takes place effectively by the anions; it is directly proportional to the anions polyhedral shape factor and inversely proportional to the squire of the bond length. The above



Fig. 1. Schematic representation of centroid shift (ε_c) and its influence on Ce³⁺ 5 d to 4f transition in a certain phosphors host composition [51]. (Reproduced with permission from ref. 51, copyright 2017, Royal Society of Chemistry).

excitation and emission in a desired spectral region.

2.1.1. Centroid shift

The centroid shift of the 5 d centroid energy of the divalent Eu^{2+} or trivalent Ce^{3+} activators is 51,230 cm⁻¹ (6.35 eV) [48–50]. The 4f – 5 d spin allowed transition of the trivalent Ce^{3+} activators attributed to both the centroid shift and the crystal field splitting, are shown in Fig. 1 [51]. The phenomenon behind the centroid shift and its origin in the host lattice of different phosphors is correlated with the covalence and polarizabilities characteristics of the activated Ce^{3+} anion coordination [49,52]. The 5 d centroid shift (ε_c) for the activated Ce^{3+} ions can be demonstrated by the model showing the associated motion between the 5 d electron and the ligand electrons [48,53],



parameters have the most essential role in the emission band redshift [5]. Due to the reduction of the 5 d level centroid shift and the neplhelauxetic effect, which occurs due to the expansion of the host lattice and the less covalent character, the substitution of small Si–N by large Al–O typically results in the blue shift [5,56–58].

However, the Stokes shift seems to play a significant role in the shift of photoluminescence emission peaks towards longer wavelengths (redshift) in the case of highly rigid crystal structure host lattice. More specifically, the pure nitride $Ba_2Si_5N_8$ phosphors have a rigid crystal structure, which is very tightly bound to the luminescence center (Eu²⁺) activator. A significant Stokes shift for $Ba_2SI_4AlN_7O:0.02Eu^{2+}$ (8013 cm⁻¹) is produced when expansion occurs in the host lattice as a result of the substitution of larger Al–O for smaller Si–N in $Ba_2Si_5N_8$ phosphors, resulting in a measurable redshift in the PL spectrum [5].

2.1.3. Crystal field splitting

In phosphors, crystal field splitting (CFS) means that the energy difference between the lowest and highest 5 d energy levels is due to the comprehensive mechanism of multiple factors, such as bond lengths along with the site coordination setting and symmetry. The strong crystal field splitting and the nephelauxetic effect efficiently tune the emission wavelength. As already discussed, the partial or complete nitrogen substitution of SiO₄ contributes to the efficient tuning of the emission color to a higher wavelength region in Eu²⁺ doped nitride and oxynitrides. More precisely, the trivalent N³⁻ (x = 3.04) covalence degree is higher than that of the divalent O²⁻ (x = 3.44), resulting is a greater nephelauxetic effect and triggering a redshift in photoluminescence excitation and emission [59].

Wang and co-workers [38] efficiently tuned the luminescence characteristics by using different cation substitutions that cause crystal field splitting variances and Stokes shift. More specifically, various UCr₄C₄ type compounds, such as CsKNa_{2-y}Li_y(Li₃SiO₄)₄:Eu²⁺ and CsKNa₂(Li₃ Si_{1-z}Ge_zO4)4:Eu²⁺ lithosilicate phosphors, have been synthesized and demonstrated the existence of three distinct crystallographic sites for activator occupation, such Na, K, and Cs. The luminescence characteristics of the Eu²⁺ ions were modified by using crystal site engineering.

To effectively regulate the migration of the activated Eu^{2+} from the accessible crystallographic site of K to the Na crystallographic sites, Li⁺ ions were added. This substitution resulted in the efficient tuning of the narrow band cyan emission at 485 nm with 27 nm FWHM to green emission centered at 526 nm with 58 nm FWHM. In addition, the local

lattice variation induced by the introduction of Li^+ ions boosted the PLQYs from 39 to 82%. Furthermore, Ge^{4+} was added to replace Si^{4+} to compensate for the shrinkage of Na polyhedron, resulting in the shoulder band of the higher wavelength of the green color emission of the doped Eu^{2+} to be gradually disappeared. The blue shift that occurred was due to the synergistic effect of crystal field splitting and Stokes shift reduction.

As a result, an efficient blue-emitting $CsKNa_2(Li_3GeO_4)_4:Eu^{2+}$ phosphor was produced, showing only one peak at 458 nm with 26 nm of FWHM. The variation of the local crystal structure with successful substitution of the higher ionic radius Ge⁴⁺ for smaller ionic radius Si⁴⁺ ions, shown in Fig. 3a, leads to Si tetrahedra expansion and further demonstrates the mechanism of the blue shift (cyan \rightarrow blue) of the emission spectrum and the disappearance of the green emission color (526 nm). However, the SiO₄ tetrahedra expansion should increase the pressure around the crystallographic site of Na, which is surrounded by four LiO₄ tetrahedra and four SiO₄ tetrahedra. In addition, the NaO (Na-O) bond length shows a decreasing trend from 2.54075 to 2.51954 and 2.41317 Å for CsKNa₂(Li₃SiO₄)₄: Eu²⁺ to CsKNa₂(Li₃Ge_{0.5}Si_{0.5}O₄)₄: Eu²⁺, and CsKNa₂(Li₃GeO₄)₄: Eu²⁺ phosphors hosts, respectively, indicating a shrinkage in the Na hexahedron. In such a small Na hexahedron, it is difficult for the divalent Eu^{2+} ions to be activated. The shoulder in the green color emission band at 526 nm was finally disappeared. On the other hand, the bond length of Cs-O and K-O shows an increasing trend that establishes a decrease in crystal field splitting with increasing Ge⁴⁺ concentration, as shown in Fig. 3b, causing a blue shift in the emission color, as shown in Fig. 3c.

2.2. Structural modifications which cause luminescence tuning

The so-called metal/rare earth activated phosphors are largely used as luminescence materials, where dopants are the sensitizers and the activators in an effective host lattice [60]. The variation in the composition and the concentration of the dopants is the easiest strategy to achieve tunable luminescence to the desired color region. Owing to the different energy level structures of the doped activators ions, different dopants absorb different energy photons from the supplied energy, which emit their unique wavelengths [13,61]. In the rare earth/metal ions activated luminescence materials, tunable photoluminescence induced by the phosphors host compositions has also been documented. For example, with different peaks being attributed to variation



Fig. 3. (a) Variation of crystal structure with efficient substitution of Ge^{4+} for Si^{4+} ions in $CsKNa_2(Li_3Si_{1-z}Ge_2O_4)_4$:0.02Eu²⁺ silicate phosphors, (b) schematic representation of the energy level of $CsKNa_2(Li_3Si_{1-z}Ge_2O_4)_4$:0.02Eu²⁺ silicate phosphors, and (c) the CIE chromaticity coordinate diagram along with digital photographs of $CsKNa_2$.yLi_y(Li_3SiO_4)_4:0.02Eu²⁺ and $CsKNa_2(Li_3Si_{1-z}Ge_2O_4)_4$:0.02Eu²⁺ silicate phosphors [38]. (Reproduced with permission from ref. 38, copyright 2019, American Chemical Society).

generated in the crystal structure due to the expansion occurred in the host lattice of phosphors composition, Eu^{2+} doped phosphors with a different composition due to the substitution of Al–O for Si–N in Ba₂Si₅N₈ (Ba₂Al_xSi_{5-x}N_{8-x}Ox) were studied [5]. More interestingly, the expansion in the host lattice of phosphors composition not only tunes the color of photoluminescence emission but also increases luminescence intensity and thermal stability. Similarly, using different compositions, such as Ca_xBa_(9-x)Lu₂Si₆O₂₄ and Sr_yBa_(9-y)Lu₂Si₆O₂₄ phosphors was achieved in our previous work [62,63]. In the photoluminescence excitation and emission spectra, the tuning affect was more precise due to differences in coordination, in active ion anions distances and the corresponding angles among them.

2.2.1. Modifications of chemical composition and crystal structure

Luminescent phosphors are essential materials in the development of solid-state lighting (SSL), display backlighting, biomarkers, and sensors [1,64]. Due to the widely varying technological applications of these luminescence materials, new phosphor compositions are highly desired and are pursued through multiple techniques, such as screening with combinatorial chemistry, cationic/anionic substitutions, and the method of single-particle diagnoses [46,65,66]. The discovery of an appropriate phosphor host lattice and crystal structure is essential for the development of the targeted rare earth (RE) activated phosphors and the manufacturing of white light-emitting diodes (white-LEDs) [67,68]. The development and investigation of new solid-state materials (inorganic phosphors) with high photoluminescence characteristics with excellent structural and thermal stability have been the subject of several research studies. In addition, different criteria may be used to determine the suitability of phosphors, such as (i) the high photoluminescence quantum efficiency achieved by optimizing the synthesis and chemical condition, (ii) the appropriate peak position achieved by the alteration of the crystal structure, the type of ions, and the surrounding environment of the activated doping, and (iii) the improved thermal stability with efficient modifications of chemical composition along with introducing defects and adjustment of the cations ordering [69]. The effect of the various cation/anion substitutions on the luminescence tuning of UCr₄C₄ type phosphors doped with divalent Eu²⁺ activator with spin allowed transition will be reviewed in this section. The discovery of the highly efficient narrow-band phosphors that crystallized in the tetragonal framework with I4/m space group is owed to the UCr₄C₄ type structure. The new Sr [LiAl₃N₄]: Eu^{2+} and Sr [Mg₃SiN₄]: Eu^{2+} nitride phosphors based on this structure were first developed by Schnick's group [21,70].

Due to its highly compact and rigid structure along with highly symmetric activated sites, these Eu^{2+} activated nitride phosphors display an efficient red emission at 615 nm with 43 nm FWHM. It was the group of Prof. Xia that recently introduced the silicate family compounds of the UCr₄C₄ type structure [4,71]. More specifically, the produced RbLi(Li₃SiO₄)₂:Eu²⁺ and RbNa₃(Li₃SiO₄)₄:Eu²⁺ phosphors emit efficient green (530 nm with 43 nm FWHM) and cyan (471 nm with 22.4 nm FWHM) color emissions with superior photoluminescence characteristics and excellent thermal stability [32].

Accordingly, different luminescence characteristics were seen, compared to the already produced $M_4(Li_3SiO_4)_4$ lithosilicate phosphors with various alkali metal cations, i.e. M = Cs, Rb, K, Na, and Li. In addition, the mechanism of the substitution and the alteration of the local structure is an important part of modifying the luminescence characteristics of the already known phosphors. This study inspired Zhao et al. [34] and produced RbNa₂K(Li₃SiO₄)₄:Eu²⁺ and CsNa₂K (Li₃SiO₄)₄:Eu²⁺ lithosilicate phosphors by successful replacing of Na⁺ with K⁺ in RbNa₃(Li₃SiO₄)₄ and then by replacing Rb⁺ with Cs⁺ ions [72]. Fig. 4 a-c illustrates the structure formation with successful cation substitutions along with X-ray diffraction profile and the symmetry of each crystallographic cationic site. The RbNa₂K(Li₃SiO₄)₄:8%Eu²⁺ and CsNa₂K(Li₃SiO₄)₄:8%Eu²⁺ lithosilicate phosphors photoluminescence

emission spectra display a narrow band cyan color emission (Fig. 4d and e), with a maximum at 480/485 nm and 26 nm of FWHM. Besides, a small shoulder peak was also observed at a higher wavelength at around 530 nm, which is also seen in both samples. In addition, compared to the photoluminescence emission peak at 471 nm of RbNa₃(Li₃SiO₄)₄:Eu²⁺ lithosilicate phosphors, which is due to the combined effect of centroid shift, Stokes shift, and crystal field splitting, shown in Fig. 4f, a slight red shift of around 10-15 nm was also observed. The effect of the concentration of Eu²⁺ on the luminescence intensity was investigated in detail. Fig. 4g and h shows that the optimum Eu^{2+} concentration was 8% in both RbNa₂K(Li₃SiO₄)₄:Eu²⁺ and CsNa₂K(Li₃SiO₄)₄:Eu²⁺ lithosilicate phosphors. The normalized photoluminescence excitation and emission spectra of RbNa₃(Li₃SiO₄)₄:8%Eu²⁺, RbNa₂K(Li₃SiO₄)₄:Eu²⁺ and CsNa₂K(Li₃SiO₄)₄:Eu²⁺ lithosilicate phosphors are compared in Fig. 4i and j, which indicate a strong red shift in both the excitation and emission spectra.

Photoluminescence emission tuning and excellent temperature stability of phosphors are of great importance for high-power white-LEDs applications. The effect of the variation of composition and structure on the thermal stability of phosphors has been extensively investigated. The RbNa₂K(Li₃SiO₄)₄:8%Eu²⁺ and CsNa₂K(Li₃SiO₄)₄:8%Eu²⁺ lithosilicate phosphors temperature-dependent photoluminescence spectra were measured in a wide temperature range from RT to 250 °C. In Fig. 5a–d the results for both samples are plotted and they show that both phosphors demonstrate excellent thermal stability. More precisely, the thermal quenching of RbNa₂K(Li₃SiO₄)₄:8%Eu²⁺ lithosilicate phosphors is lower than that for CsNa₂K(Li₃SiO₄)₄:8%Eu²⁺ lithosilicate phosphors.

The integrated photoluminescence intensity decreases to 79% of the initial intensity reported at room temperature (RT) for CsNa2K (Li₃SiO₄)₄:8%Eu²⁺ lithosilicate phosphors at the highest tested temperature of 250 °C, while decrease was only 95% for RbNa2K $(Li_3SiO_4)_4:8\%Eu^{2+}$, as shown in Fig. 5e. In addition, the activation energy (ΔE), shown in the inset of Fig. 5e, shows a decrease from 0.290 to 0.219 eV, suggesting that the thermal quenching occurred more quickly as a result of the Cs⁺ cation replacement of Rb⁺. The configuration coordinates diagram shown in Fig. 5f was used to interpret this phenomenon. In general, the 4f electrons under different energy excitation move to the 5 d excited state (line OA). The excited electrons are relaxed to the lowest 5 d state, which then returns by radiative recombination to the 4f ground state following the line BC. The luminescence center placed at the excited state will shift to the crossing point following the line BD when the temperature rises, which then returns to the ground state following the line DC, resulting in thermal quenching, also called as thermally enabled crossover process [34,73]. The greater the value of the displacement between the ground state and excited states (ΔR), the smaller the Stokes shift between 4f-5d absorption and 5 d-4f emission, opposing the luminescence center to hit the crossing point [74].

2.3. Selecting or change of a suitable crystallographic site for the activators

The most significant feature of rare earth (RE) doped phosphors is the adjustment of the crystallographic site of the dopants through the modification of the chemical composition to improve and optimize the photoluminescence characteristics.

By applying the crystal-site engineering approach, excellent results have been obtained. For example, the green-emitting $\alpha_L - Ca_2SiO_4:Eu^{2+}$ phosphor was tailored to red-emitting phosphors, and the order of SiN₄ and AlN₄ cluster in (CaSr)SiAlN₃:Eu²⁺ increased the luminescence intensity [75,76]. Therefore, the presence of multi-crystallographic sites in the host lattice of phosphors provides several opportunities to tune the luminescence by designing the activators surrounding environment. More specifically, due to a possible mismatch between the activator and the host lattice cation at a specific crystallographic site, the activator should ideally occupy the most suitable site [77]. This means that, by increasing the doping concentration, the luminescence can be efficiently



Fig. 4. Various structural and composition characteristics. (a) Schematic illustration of the phosphors composition transformation from the RbNa₃(Li₃SiO₄)₄ compound to RbNa₂K(Li₃SiO₄)₄ and CsNa₂K(Li₃SiO₄)₄ phosphors compositions with various cations substitution. (b) X-ray diffractograms (XRD) of the RbNa₂K(Li₃SiO₄)₄ and CsNa₂K(Li₃SiO₄)₄ lithosilicate phosphors compositions along with standard PDF card number 82-0817. (c) The surrounding coordination polyhedral environment of Na1, Na2, K1, Rb, and Cs crystallographic sites and crystal structure of the various samples. (d and e) Photoluminescence emission spectra of the optimum RbNa2K $(\text{Li}_3\text{SiO}_4)_4{:}8\%\text{Eu}^{2+}$ and $\text{CsNa}_2\text{K}(\text{Li}_3\text{SiO}_4)_4{:}8\%\text{Eu}^{2+}$ lithosilicate phosphors. (f) Schematic illustration of the centroid shift, Stokes shift, and crystal field splitting. (g and h) Influence of Eu²⁺ concentration in RbNa₂K(Li₃SiO₄)₄:8%Eu²⁺ and CsNa₂K $(Li_3SiO_4)_4:8\%Eu^{2+}$ lithosilicate phosphors. (i and j) Comparison of the normalized photoluminescence excitation and emission spectra of RbNa₃(Li₃SiO₄)₄:Eu²⁺, RbNa2K(Li3SiO4)4:Eu2+ and CsNa₂K(Li₃SiO₄)₄:Eu²⁺ phosphors [34]. (Reproduced with permission from ref. 34, copyright 2019, Wiley).



Fig. 5. Influence of temperature on luminescence characteristics (under 395 nm excitation) of (a) $RbNa_2K(Li_3SiO_4)_4$:8% Eu^{2+} , and (b) $CsNa_2K(Li_3SiO_4)_4$:8% Eu^{2+} , (c and d) temperature dependent behavior of $RbNa_2K(Li_3SiO_4)_4$:8% Eu^{2+} and $CsNa_2K(Li_3SiO_4)_4$:8% Eu^{2+} lithosilicate phosphors, (e) comparison of the luminescence intensity decrease in the temperature range from RT to 250 °C, and (f) illustration of thermal quenching of the Eu^{2+} activators by a configuration coordinate diagram [34]. (Reproduced with permission from ref. 34, copyright 2019, Wiley).

tuned to the desired value (i.e. successful tuning can be achieved) as the activator ions are forced to join the less suitable sites in the host [75, 78–80]. Additionally, modification by cation substitution in the desired crystallographic site can also push the luminescence center to join less suitable crystallographic sites in the host lattice of multi-cation sites [77, 81–84]. For example, cation substitution shifts Eu^{2+} to non-preferential crystallographic sites in $Sr_{2-x}Ba_xSi_2O_2N_2:Eu^{2+}$ phosphors, which efficiently tunes the luminescence towards longer wavelengths [82].

Wang and his colleagues [38] developed CsKNa_{2-y}Li_y(Li₃SiO₄)₄:Eu²⁺ and CsKNa₂(Li₃Si₁₋₂Ge_zO₄)₄:Eu²⁺ lithosilicate phosphors that provide activator occupation with three distinct crystallographic cationic sites (Na, K, and Cs). In addition, the activated Eu²⁺ crystal site engineering was used to tune the luminescence feature efficiently. The Li⁺ ions were first introduced in CsKNa₂Li(Li₃SiO₄)₄:Eu²⁺ phosphors to move the activated Eu²⁺ from K to Na crystallographic site to efficiently tune the narrow band cyan emission ($\lambda_{em} = 485$ nm with 27 nm FWHM) to the narrow band green color emission ($\lambda_{em} = 526$ nm, with 58 nm FWHM). In Fig. 6a – c the crystal structure along with the schematic diagram of the Li⁺ substitution leading to the improvement of the Eu²⁺ occupation in the Na crystallographic site are illustrated more precisely.

The Eu²⁺ activator luminescence characteristics can be greatly influenced by the ambient environment in the phosphors host lattice because the Eu^{2+} 5 d state is sensitive to the surrounding environment, leading to high crystal field splitting of the external 5 d orbitals [85]. To change the luminescence features, the Li⁺ cations are substituted to effectively alter the local lattice. In Fig. 6d and e, the PLE spectra of CsKNa_{2-x}Li_x (Li₃SiO₄)₄:0.02Eu²⁺ lithosilicate phosphors monitored at 485 nm and 526 nm emission wavelength shows that the excitation occurs within wide band with small peaks ranging from 240 to 310 nm, while large peaks with a maximum at 398 nm ranging from 315 to 440 nm show a great match with the commercial near-UV emitting chip. The presence of a wide-band excitation is due to the transition from the 4f [7] ground state to the 4f [6]5 d excited state of the activator Eu^{2+} [46]. In addition, the effect of the Li⁺ ions concentration on the photoluminescence excitation was shown in Fig. 6f, which indicates that the intensity of photoluminescence excitation first increases with an increase in Li^+ concentration up to y = 0.2, while a further increase for y > 0.2 induces a decrease in the intensity of photoluminescence excitation, which is due to movement of the activated Eu^{2+} ions to other available crystallographic sites.

A narrow band emission (440-660 nm) under an excitation at 398 nm is shown in the photoluminescence emission spectra illustrated in Fig. 6g. The emission spectrum consisted of a double emission band with a maximum peak at 485 nm and the presence of two luminescence centers in CsKNa_2.yliy (Li_3SiO_4)_4:0.02Eu^{2+} lithosilicate phosphors was further validated at 526 nm. Furthermore, the lower wavelength emission peak at 485 nm (cyan emission color) was dominant at the lower Li⁺ concentration (Li $^+$ < 0.5), while the green emission color peak at 526 nm was dominant at the higher Li^+ concentration (Li > 0.5). The emission peak at 485 nm and the peak at 526 nm was almost equal in intensity when Li^+ concentration was exactly at y = 0.5. With increased Li^+ ion concentration, the occupation of the Eu^{2+} site in the next available crystallographic site should increase. Both Eu²⁺ occupied crystallographic sites have different surrounding environments that result in a different color emission from different crystal field splitting of the 5 d excited state of Eu^{2+} dopants.

The lower temperature (77 K) photoluminescence emission spectrum of the initial sample $CsNa_2K(Li_3SiO_4)_4$:0.02Eu²⁺ with y = 0 was deconvoluted into three Gaussian peaks to further confirm the occupation of Eu²⁺ at different crystallographic sites, as shown in Fig. 6h, which indicates that two emission peaks are very close to each other, attributed to the occupation of Eu²⁺ at identical cuboid sites. As shown in Fig. 6a, three crystallographic sites (higher symmetric Cs and K and lower symmetric Na) for the occupation of the activated Eu²⁺ ions are provided by the host lattice of CsKNa_{2-y}Li_y(Li₃SiO₄)₄ lithosilicate phosphors. The small bandwidth of the lithosilicate phosphors is due to the high symmetry and the excellent rigidity of the crystallographic cation sites of the host lattice [36]. The occupation of Eu²⁺ ions in Cs and K crystallographic sites with a strongly symmetric cubic lattice is thus attributed to peak 1 (484.6 nm) and peak 2 (485.1 nm).

The ionic radius of the eight coordinated Cs^+ ion (r = 1.74 Å) is much higher than the ionic radius of the eight coordinated K^+ ion (1.51 Å) in the activated Eu^{2+} (1.25 Å with eight coordination). The emission peak 1 (484.6 nm) is therefore attributed to the occupation of Eu^{2+} dopants in K^+ cationic sites, while the peak 2 (485.1 nm) is attributed to the occupation of Eu^{2+} in the crystallographic site of Cs^+ . The ionic radius of



Fig. 6. (a) Schematic illustration of the CsKNa₂(Li₃SiO₄)₄ phosphors host crystal structure with the orientation of the c-axis along with two separate types of the vierer ring channels and coordination of Cs, K and Na polyhedra at CsKNa₂(Li₃SiO₄)₄ phosphors host sites, (b) comparison of structural configuration of CsKNa₂(Li₃SiO₄)₄ and CsKNa₁(Li₃SiO₄)₄ phosphors host lattices, (c) schematic diagram of Eu²⁺ redistribution at K and Na sites, (d, e) PLE spectra of the CKNa_{1.98-y}Li_y(Li₃SiO₄)₄;0.02Eu²⁺ ($0 \le y \le 1$) phosphors at various monitored emission wavelengths, (f) relative excitation strength vs various Li⁺ contents (y) at λ_{em} = 485 nm and $\lambda_{em} = 526$ nm, (g) PL spectra of CKNa_{1.98-y}Li_y(Li₃SiO₄)₄;0.02Eu²⁺ ($0 \le y \le 1$) phosphor at 75 K, and (i) representative CsKNa_{1.98}(Li₃SiO₄)₄;0.02Eu²⁺ phosphors decay time profile at $\lambda_{ex} = 398$ nm, $\lambda_{em} = 526$ nm, (a) (Reproduced with permission from ref. 38, copyright 2019, American Chemical Society).

the doped Eu^{2+} is similar to K⁺ ionic radius; so, the peak associated to the K⁺ occupation is dominant; while the peak associated to the Cs⁺ crystallographic site occupation of Eu^{2+} is negligible. The input of the doped Eu^{2+} ions to the lower symmetry crystallographic site of Na⁺ is attributed to peak 3 (526 nm), which is the peak at the higher wavelength region (green color region). From the measurements of the photoluminescence decay time of CsKNa(Li₃SiO₄):Eu²⁺ lithosilicate phosphors, the presence of more than one crystallographic site has been further confirmed. As shown in Fig. 6i, the decay time measurement under excitation of 398 nm with controlled emission peaks at 485 nm and 526 nm shows two different decay times at 0.56 μs (for 485 nm) and 0.93 μs (for 526 nm), which further verified the two different luminescence centers in CsKNa_2.yLi_y(Li_3SiO_4)_4:0.02Eu^{2+} lithosilicate phosphors. Thus, it was possible to control the selection of crystallographic sites for being occupied by the activated Eu^{2+} ions by substituting Si^{4+} ions for tetravalent Ge^{4+} ions. The X-ray diffraction (XRD) pattern along with the crystal structure of CsKNa_2(Li_3Si1_2Ge_2O_4)_4: 0.02Eu^{2+} (0 \leq z \leq 1) lithosilicate phosphors are shown in Fig. 7a.



Fig. 7. (a) X-ray diffractograms of CsKNa₂(Li₃Si_{1-z}Ge_zO₄)₄:0.02Eu²⁺ ($0 \le z \le 1$) along with the patterns of the standard card of CsKNa₂(Li₃SiO₄)₄ (ICSD no. 74864), (b, c) CKNa₂(Li₃Si_{1-z}GzO₄)₄:0.02Eu²⁺ ($0 \le z \le 1$) ($\lambda_{ex} = 398$ nm) normalized PLE and PL spectra, (d) PLE and PL spectra of the optimized CsKNa_{1.98}(Li₃GeO₄)₄:0.02Eu²⁺, (e) photoluminescence decay curves of CsKNa(Li₃Si_{1-z}Ge_zO₄)₄:0.02Eu²⁺ ($0 \le z \le 1$) phosphors, where the inset shows the lifetime for various contents of Ge⁴⁺ [38]. (Reproduced with permission from ref. 38, copyright 2019, American Chemical Society).

The result of the Ge⁴⁺ substitution of the crystal structure of CsKNa₂(Li₃Si_{1-z}Ge_zO₄)₄: 0.02Eu²⁺ lithosilicate phosphors suggested that all the X-ray diffraction peaks march well to the standard CsKNa₂(Li₃SiO₄)₄ lithosilicate phosphors peaks (ICSD no 74864), confirming the development of the pure phase even for a complete substitution of Ge⁴⁺ for Si⁴⁺ ions. In addition, at the left-hand side of Fig. 7a, a shift was observed at the XRD peaks at $2\theta = 22.5^{\circ}$ towards the small-angle direction, confirming the expansion of the host lattice with the efficient substitution of the high ionic radius of the four coordinated Ge⁴⁺ ions (R = 0.39 Å) with smaller ionic radius of the four coordinated Si⁴⁺ ions (R = 0.26 Å). Fig. 7b and c demonstrate the normalized room temperature photoluminescence excitation and emission spectra of CsKNa₂(Li₃Si₁-zGe₂O₄)₄:0.02Eu²⁺ lithosilicate phosphors.

The photoluminescence excitation is a wide band spectrum ranging from 250 to 430 nm due to the typical 4f – 5 d spin allowed transitions of the activated Eu²⁺ ions. The photoluminescence emission spectrum shown in Fig. 7c indicates that the increasing concentration of Ge⁴⁺ ions in CsKNa₂(Li₃Si_{1-z}Ge_zO₄)₄:0.02Eu²⁺ lithosilicate phosphors results in a blue shift from the cyan emission (485 nm) to the blue color region with a maximum peak at 485 nm in the lower wavelength region. In addition, with the introduction of Ge⁴⁺ ions, the higher wavelength peak (526 nm) around the green emission color gradually disappears. A small and symmetric band blue emission was thus reported and plotted in Fig. 7d at z = 1 in CsKNa₂(Li₃Si_{1-z}Ge_zO₄)₄:0.02Eu²⁺ lithosilicate phosphors, with a maximum peak at 458 nm with 26 nm FWHM. For applications of wide color gamut backlighting and high-power white LEDs, the apparent narrow-band blue emission is a remarkable improvement [86].

The effect of Ge⁴⁺ concentration on the photoluminescence decay time profile was tested at different monitored wavelengths. The results plotted in Fig. 7e show that the decay time decreased from 0.62 to 0.39, 0.2, 0.12, and 0.02 μs for $z=0{-}1$. The apparent decrease in decay time (inset of Fig. 7e) is consistent with the blue shift in the emission spectrum. The selection of the site of the doped Eu²⁺ activators was further confirmed by the spectral adjustment of phosphors.

In addition, the substitution of the larger ionic radius Ge^{4+} ions for the smaller ionic radius Si^{4+} ions results in the expansion of the Si tetrahedra. However, the substitution of the SiO_4 tetrahedra with four LiO₄ tetrahedra should increase the pressure in the surroundings of the Na⁺ crystallographic site. The average of both Na–O bond lengths indicate a decreasing trend from 2.54075 to 2.51954 and 2.41317 Å for z = 0, 0.5, and 1.0, respectively, favoring the Na hexahedron to shrink. In Na crystallographic sites with such a small hexahedron, it is difficult to be occupied by the activated Eu²⁺ dopants. Therefore, the higher wavelength green emission peak at 526 nm disappears. On the other hand, the crystallographic cationic sites of K/Cs are only surrounded by LiO₄ tetrahedra, which indicate shrinkage if the SiO₄ tetrahedra of the crystallographic site of Na contribute to an increase in the distance between the crystallographic sites of Si⁴⁺ and K/Cs. The average K–O and Cs–O bond lengths are therefore increased, from 2.82770 to 2.83660 and 2.88361 Å for K–O, and from 3.11838 to 3.14754 to 3.28215 Å for Cs–O. The crystal field strength of the host lattice of the phosphors can be determined by the following equation [87–91],

$$D_q = \frac{z \, e^2 r^4}{6R^5} \tag{2}$$

where R is the distance from the central ion to its ligands, D_q is crystal field splitting, e is the electron charge, and z' the valence or the charge of the anion. As discussed above, the narrow-band emission is due to the occupation of Eu²⁺ in the crystallographic sites of K/Cs and the average bond length of K–O and Cs–O shows an increasing trend that leads to an increase in the distance from the central ion to its ligands (R) with an increase in the concentration of the substitute Ge⁴⁺. The value of the crystal field strength (D_q) decreases according to equation (2) along with an increase of R, leading to a decrease in the crystal field strength with an increase of Ge⁴⁺ ions in CsKNa₂(Li₃Si_{1-z}Ge_zO₄)₄:0.02Eu²⁺ lithosilicate phosphors. In addition, the Stokes shift may be another important reason for the major blue shift shown in Fig. 7d. The Stokes shift was observed to decrease gradually with a rise in Ge⁴⁺ concentration, which raised the 5 d state of the doped Eu²⁺ ions.

2.4. Control of crystalline phase transition

Multiple white-light-emitting phosphors have been produced, as mentioned above. The structure and luminescence features have been extensively investigated. The narrow-band emitting phosphors are attractive materials because they enhance the wide color gamut and efficiency due to their high efficiently to boost the performance of the backlighting display for the next-generation lighting applications. However, the understanding of mechanism that will ultimately allow the development of novel phosphors is still an urgent and essential necessity since it will accelerate the manufacture of white LEDs.

The development of the mineral-inspired structures of inorganic phosphors is an emerging method to produce novel luminescence materials for white-LEDs. The mineral-inspired method is based on the production of novel phases from the initial component of the prototype. More specifically, the typical mineral compounds having unique chemical formulae can be considered as the primary prototype compounds, which highly inspired people to develop new phases by using various cationic/anionic substitutions. For instance, a highly efficient narrow-band red-emitting Sr(LiAl₃N₄):Eu²⁺ nitride phosphors with UCr₄C₄ type structure prototype was developed [1] according to this strategy, i.e. it is a novel white LEDs phosphor with the mineral-inspired prototype model evolution and phase formation [68, 92,93] The structure of the phosphors has a high degree of condensation (k = 1) and provides cubic like crystallographic sites for the occupation by the divalent Eu²⁺ ions. However, the previous UCr₄C₄ structure



Fig. 8. (a) X-ray diffractogram of RbLi(Li₃SiO₄)₂:Eu²⁺ phosphors with the standard PDF card no.76-0344 (the unidentified phases are marked by asterisk), (b) RbLi (Li₃SiO₄)₂:Eu²⁺ phosphors crystal structure with Eu²⁺ doping mechanism in a distorted RbO₈ cube with a local EuO₈ structure joined to the top and bottom of two RbO₈ cubes, Li₅O₃, Li₆O₃ nodes triangles, Li₁O₄, Li₂O₄, si₁O₄, and Si₂O₄ tetrahedra along the b-axis, and the RbO₈ and EuO₈ cubes shape an infinity column, (c) the DFT-PBE method determined band structure of the RbLi(Li₃SiO₄)₂:Eu²⁺ phosphors host, and the inset shows a digital photograph of the optimized sample, (d) complete and orbital projected DOSs for RbLi(Li₃SiO₄)₂:Eu²⁺ obtained with the DFT-PBE process, (e) PLE and PL spectra of RbLi(Li₃SiO₄)₂:Eu²⁺ and the commercial β -SiAlON:Eu²⁺, (f) the decay curve of the optimized phosphors sample under the excitation of 460 nm and monitored emission of 530 nm, (g, h) temperature dependence of the PL spectra of the optimized sample under an excitation at 460 nm in the temperature range of RT - 250 °C with a temperature step of 25 K, and (i, j) the PL spectra along with digital images (under 365 nm UV lamp) of the pristine RbLi(Li₃SiO₄)₂:8%Eu²⁺ phosphors and the ambient atmosphere samples at various times [36]. (Reproduced with permission from ref. 36, copyright 2018, Wiley).

prototype investigation focused only on the design of nitride phosphors that give a narrow-band red emission due to their highly condensed and rigid framework structure [22]. However, as phosphors host lattice, the oxide-based composition of the UCr₄C₄ type structure, such as NaLi₃SiO₄ and CsNa₃PbO₄ silicate phosphors, is poorly investigated [1,68].

The new phase formation of UCr₄C₄ type compounds, such as Na (Li₃SiO₄]:Eu²⁺ (tetragonal space group of *I*4₁/*a*), K(Li₃SiO₄]:Eu²⁺ (triclinic space group with PĪ), and NaK₇ [Li₃SiO₄]₈:Eu²⁺ (tetragonal space group *I*4₁/*a*) lithosilicate phosphors, were developed by Dutzler and coworkers [94]. The developed phosphors exhibit various attractive luminescence characteristics, such as the ultra-narrow-band blue emission of the Eu²⁺ doped Na [Li₃SiO₄] phosphors, while K [Li₃SiO₄]₈:Eu²⁺ exhibits a broad-band yellow emission, and the NaK₇ [Li₃SiO₄]₈:Eu²⁺ lithosilicate phosphors exhibits a double band yellow–green emission under the excitation of near – UV to blue light. In addition, Zhao et al. [36] synthesized a highly efficient green color emitter RbLi(Li₃SiO₄)₂: Eu²⁺ lithosilcate phosphor from the structure of the highly condensed and rigid framework of UCr₄C₄ type compound for the next-generation narrow-band emission.

Superior photoluminescence characteristics, such as an unprecedented narrow-band green color emission peaking at 530 nm with 42 nm FWHM under 460 nm blue light irradiation, were achieved from phosphors of the oxide family. The narrow-band green emission achieved is superior to the commercially available β -SiAlON phosphors. Both theoretical and experimental methods were used to investigate the origin of the narrow-band emission. The X-ray diffraction (XRD) measurements, along with structure assessment, confirmed the phase formation and the high purity. This findings, plotted in Fig. 8a and b, show that the main peaks of XRD match well with the standard PDF card number 76–0344; small impurity peaks are also observed [95]. A highly condensed and rigid framework with k = 1 (Li₃Si:O₄ = 1) degree of condensation is suggested by the crystal structure (Fig. 8b) of the RbLi (Li₃SiO₄)₂:Eu²⁺ phosphors. In eight coordinated Rb ⁺ cations, the Eu²⁺ ions have been doped, as is also seen in Fig. 8b.

Using the density functional theory (DFT) and Perdew Burke Ernzerh (PBE) method, the characteristic band structure along with total and projected state densities (DOS) measurement of the developed RbLi (Li₃SiO₄)₂ phosphor host lattice were calculated. Fig. 8c and d shows that the formed RbLi(Li₃SiO₄)₂ host lattice has a stable structure and provides a sufficient band gap for the occupation by the divalent Eu²⁺ activators. The measured band-gap and the DOS outcomes are shown in Fig. 8c and d. In the produced RbLi(Li₃SiO₄)₂:8%Eu²⁺ lithosilicate phosphors, the room temperature photoluminescence excitation and emission spectra were measured and compared to the commercially available green-emitting β-SiAlON phosphors. The photoluminescence excitation (Fig. 8e) is a broad-band ranging from 300 nm to 530 nm with different peaks that confirm that the excitation band of the developed lithosilicate phosphor is suitable for the commercially available UV and blue-emitting chips.

Under 460 nm excitation and 530 nm monitoring emission wavelength, the photoluminescence decay time profile of RbLi(Li₃SiO₄)₂:8% Eu^{2+} lithosilicate phosphors was recorded. Fig. 8f shows the photoluminescence decay time profile, which can be well fitted by using a single exponential component, as shown in equation (3) [96],

$$I(t) = I_0 + Aexp(-t/\tau)$$
(3)

Where the photoluminescence intensities at times t = t and t = 0 are I(t) and I₀, respectively, A is the exponential constant, and τ is the exponential decay time component. Thus, the decay value of RbLi (Li₃SiO₄)₂:8%Eu²⁺ lithosilcate phosphors was determined as 0.84 µs, by using these fitting results (Fig. 8f) and exponential constants. The narrow-band green emission originated from the Eu²⁺ occupied single crystallographic site (Rb), which is also consistent with the photoluminescence emission spectrum (Fig. 8e) as shown above. This is validated by the well-fitting with one exponential component and the

shape of the exponential decay curve.

Temperature stability is an important parameter influencing photoluminescence performance in several applications. It is, therefore, necessary to investigate the thermal quenching behavior along with the stability of chromaticity of the developed green-emitting RbLi (Li₃SiO₄)₂:8%Eu²⁺ lithosilicate phosphors in detail. The temperature dependence of PL and the chromaticity stability of the broad temperature range (from RT to 250 °C with 25 K interval) are illustrated in Fig. 8g and h. The findings show that the intensity of the emission spectrum decreases with the increase of temperature. The intensity of the maximum green color emission peak (530 nm) of the RbLi (Li₃SiO₄)₂:8%Eu²⁺ lithosilicate phosphors decreased to 92.4% at 150 °C, i.e. a loss of 7.6% was recorded compared to the 530 nm emission peak intensity at room temperature.

It was also examined the chemical stability of RbLi(Li₃SiO₄)₂:8% Eu^{2+} lithosilicate phosphors in detail. Therefore, the photoluminescence spectra of the pristine RbLi(Li₃SiO₄)₂:8% Eu^{2+} lithosilicate phosphors sample and the photoluminescence spectra of the RbLi(Li₃SiO₄)₂:8% Eu^{2+} samples after exposure to ambient atmosphere for 1, 3, 5, and 7 days were recorded. The findings, shown in Fig. 8i and j, suggest that in the exposed samples, the integrated emission intensity decreases to 93%, 86%, 74%, compared to the pristine RbLi(Li₃SiO₄)₂:8% Eu^{2+} phosphors sample intensity. Fig. 8j displays the digital photograph under natural daylight and the excitation with 365 nm UV light of the pristine sample and the exposed samples. Compared to the exposed samples, the pristine sample shows higher brightness, suggesting that the stability of the phosphors need to be further improved by using surface coating and passivation techniques, as seen in other phosphor systems [97].

3. Development of $U\mathrm{Cr}_4\mathrm{C}_4$ type compounds for applications of white LEDs

An outstanding technological achievement is considered the technology of light-emitting diode (LED) based solid-state lighting [98]. Its market share was \$25 B in 2018. The LED lighting market is growing rapidly [Ref: www.ledmagazine.com] and it is projected to rise further in the future because lighting accounts for 20% of global electoral energy consumption. More interestingly, LEDs do not only provide general illumination service in indoor lighting but are also becoming more common for outdoor and industrial applications along with backlighting in displays and mobile devices [98,99].

Compared to traditional lighting sources, such as fluorescent tubes and incandescent lambs, the LED-based solid-state lighting has many advantages, including high energy efficiency, smaller size along with efficient color controllability, and longer life time. In addition, their use is environmentally friendly, satisfying the need for the lowest energy consumption technology, as well [100,101]. Obviously, the issue of energy use is a far more important aspect, recognizing that the consumption of this energy has a tremendous impact on global warming [100]. By using different methods, LED-based white light generation can be achieved.

The coating of yellow-emitting YAG: Ce^{3+} phosphor on a blueemitting chip is the simplest and the most commercially and widely used technique for producing effective white light [102–112]. A portion of the emitted blue light from the blue-emitting chip is absorbed by the yellow phosphors in this process, which internally emits wide band yellow light, resulting in white light in combination with the remaining portion of blue emission (unabsorbed). There is, however, a deficiency of the portion of green and red color, which leads to lower CRI <80 and high CCT >7000 K. Therefore, different methods, such as coating the combination of yellow and red emitting phosphors on the blue emitting chip, or coating of red and green-emitting phosphors on a blue-emitting chip, generates highly efficient white light with low CCT with high CRI value. Fig. 9a and b schematically illustrate the multi-colored phosphors coating on the blue-emitting chip.



Fig. 9. Schematic illustration of the fabricated light emitting device, (a) blue LED chip with yellow and red emitting phosphors, and (b) blue LED chip with green and red emitting phosphors.

3.1. White LEDs for solid-state lighting

Light-emitting diodes (LEDs) are optoelectronic devices that are commonly used in different fields, such as medical science, display technology, residential lighting, and optical communication, primarily due to their controllable emission, high performance with low operating voltage, negligible heat release, and long operating lifetime [14,62,113, 114]. Solid-state lighting (SSL) is a new technology that is used in semiconductor diodes (LEDs) to produce artificial white light with electrical current flowing within the diode (electroluminescence). SSLs are mainly categorized into three major groups, according to the semiconductor materials used for their manufacturing, which are polymers, organic, and inorganic light-emitting diodes.

Solid-state lighting (SSL) was introduced in the global market through the use of light-emitting diodes (LEDs) since it provides mercury-free emission and also features outstanding characteristics, such as low energy consumption, high quality luminescence, high durability, and superior long term working lifetime. It can cover a wide range of lighting applications, such as residential lights, architecture lighting, medical lighting, traffic signals, and sensitive lighting etcetera. These characteristics overcome all traditional lighting technologies (filament and fluorescent lamps). Hence, SSL is a promising alternative with excellent market prospects. According to a study published in 2012, the use of such emerging technologies can increase the energy efficiency by 50%, compared to the incandescent light bulb with 5% energy efficiency, and 42\$ billion can be saved by 2025 [115].

Cui et al. [116] produced an efficient red-emitting SrLiAl₃N₄:Eu²⁺ nitride phosphor of the UCr₄C₄ type compound with the addition of BaF₂ as a flux. Red emitting phosphors emitted an efficient narrow-band emission, which can overcome the deficiency of the red color emission of the commercially available YAG:Ce³⁺ yellow emitting phosphors. More interestingly, under the excitation of 455 nm blue light irradiation, the produced SrLiAl₃N₄:Eu²⁺ nitride phosphors emit a narrow emission band with a maximum emission peak at 648 nm. Fig. 10a displays the diffuse reflection spectrum along with the wide-band excitation (200–650 nm) and narrow-band red emission. The red emission color and its tuning with the increase in temperature is seen in the CIE chromaticity coordinate diagram, shown in Fig. 10b, which confirms the



Fig. 10. (a) SrLiAl₃N₄:Eu²⁺ PLE and PL spectra, and host diffuse reflectance spectrum of SrLiAl₃N₄ phosphors, (b) SrLiAl₃N₄:Eu²⁺ CIE chromaticity diagrams of 5% mol BaF2 flux at various temperatures, (c) as-fabricated w-LEDs with a 455 nm blue chip and commer-YAG:Ce³⁺ cial and as-prepared SrLiAl₃N₄:Eu²⁺ phosphors electroluminescence spectra. The insets depict the digital images of power input lamps [116]. (Reproduced with permission from ref. 116, copyright 2016, Royal Society of Chemistry).

blue shift in the emission color with temperature increase (25–200 $^\circ\text{C}\textsc{)}.$

In order to demonstrate the significance of the synthesized SrLiAl₃N₄:Eu²⁺ red-emitting nitride phosphors, white-light-emitting diodes (white-LEDs) were developed by the coating of the commercially available Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce³⁺) phosphors along with or without the addition of the synthesized red-emitting SrLiAl₃N₄:Eu²⁺ nitride phosphors on 455 nm blue light-emitting chips. Fig. 10c displays the electroluminescence spectra of the manufactured phosphors converted LEDs (pc-LEDs) within a forward-bias current of 30 mA. Three distinct emission bands at 455, 550, and 650 nm were recorded, associated with chip emission (455 nm blue emission color), YAG: Ce^{3+} (550 nm wide band yellow emission), and SrLiAl₃N₄:Eu²⁺ nitride phosphors emissions (650 nm narrow-band red emission color). The results show that less correlated color temperature (CCT = 4060 K, 3056 K) and higher CRI values (Ra 84.5, 93.4) can be obtained through the red phosphors addition. Consequently, the synthesized narrow-band emitting SrLiAl₃N₄:Eu²⁺ nitride phosphors can be a significant redcomponent phosphor for pc-LEDs.

Wang and colleagues [38] synthesized UCr₄C₄ type CsKNa_{2-y}Li_v(- Li_3SiO_4): Eu^{2+} and $CsKNa_2(Li_3SiO_4)_4$: Eu^{2+} lithosilicate phosphors, which show a tunable emission, corresponding to the Eu^{2+} occupation in three distinct crystallographic sites. White LEDs were manufactured by the representative cyan using color emitting CsKNa_{1.48}Li_{0.5}(Li₃SiO₄)₄:0.02Eu²⁺ and the green color emitting CsKNa_{0.98}Li(Li₃SiO₄)₄:0.02Eu²⁺ lithosilicate phosphors to demonstrate the potential of the developed CsKNa_{1.98-v}Li_v(Li₃SiO₄)₄:0.02Eu²⁺ lithosilicate phosphors for promising general lighting applications. More specifically, the combination of cvan-emitting CsKNa_{1.48}Li_{0.5}(Li₃SiO₄)₄:0.02Eu²⁺ lithosilicate phosphors and the red-emitting CaAlSiN₃:Eu²⁺ phosphors were coated on the 370 nm UV emitting chip.

The electroluminescence of the fabricated light-emitting diodes was measured under the applied voltage of 3.15 V and 20 mA current. The results are plotted in Fig. 11a, which demonstrate the generation of high quality warm white light with high color rendering index (CRI = 84), color coordinates of (0.4022, 0.4187), and lower correlated color temperature (CCT = 3084 K). The produced CsKNa_{0.98}Li (Li₃SiO₄)₄:0.02Eu²⁺ green-emitting lithosilicate phosphors along with the combination of blue-emitting BaMgAl₁₀O₁₇:Eu²⁺ and red-emitting CaAlSiN₃:Eu²⁺ phosphors were coated on a 370 nm UV light-emitting chip.

Fig. 11 b shows the electroluminescence spectrum under the same applied voltage (3.15 eV) and current (20 mA). High quality warm white light was produced with a higher CRI value of 95.8, color coordinates of (0.3315, 0.3750), and low CCT of 5045 K. In addition, the manufactured trichromatic white LED displays superior luminous efficacy of 94.16 lm W^{-1} . Therefore, the manufactured devices, shown in Fig. 11a and b, demonstrate the superior performance of lithosilicate phosphors, emitting cyan and green color, showing potential for applications in the near-UV LEDs.

3.2. White LEDs for displays back lighting

The display technology has been widely introduced in our lives due to its wide range of applications, such as smartphones, laptops, computers, long screen television (TV), and data projectors. along with versatile flexible display [1,117]. The light-emitting diode-based solid state lighting has recently been used as backlighting in liquid crystal displays (LCDs), which are the driving force in the display industry. In addition, quantum dots (QDs) based LEDs, micro-LEDs, and organic LEDs are also very promising in the display technology [117–120]. Accordingly, the method for producing LCDs is very important in display technology, which is directly related to durability and cost [117,121]. However, traditional LCD backlighting units are unable to fulfill the demand of the wide color gamut for color visualization since customers are attracted towards natural color. Therefore, for the advancement in LCD technology, it is highly needed to produce broad color gamut backlights.

There are three types of backlights which can be used in order to achieve a wide color gamut backlights. The first is the multichip white LEDs obtained from the red, green, and blue (RGB) LEDs mix, the second is LEDs based on QDs, and the third is phosphors-converted LEDs. The multichip LEDs and QDs LEDs show excellent tuning ability and exhibit superior quantum efficiency. The multi-chip white LEDs suffer from the different degradation rates of the RGB LEDs, which is the low efficiency of the green LED chips, called as green gap. In addition, the extremely complex chip-driven device leads to a high-cost product that decreases the prospect of multichip LEDs in practical applications.1 Because of its outstanding narrow-band emission with high PLQYs, the QDs based LEDs show remarkable potential as a next-generation wide color gamut display [122,123]. However, during the production of LED devices, it is very difficult to preserve and maintain the characteristics of the components. In addition, the long-term operating lifetime is another issue in QDs LEDs-based displays. Furthermore, the cost of LED displays based on QDs is very high, making it affordable only for a high class of customers. Therefore, due to their cost-effectiveness, robustness, and high performance, phosphors-converted LEDs are often used for the manufacturing of displays compared to multichip and QDs based LEDs.

The commercially available phosphors converted white LEDs composed of a combination of green-emitting β -SiAlON:Eu²⁺ and redemitting K₂SiF₆:Mn⁴⁺ phosphors with blue-emitting InGaN chip are promising white LEDs for backlighting LCDs [1]. Compared to cold cathode based fluorescence lamps (72% NTSC), this combination of narrow-band green and red-emitting phosphors along with blue-emitting chip results in phosphors converted LEDs based displays that show a wide color gamut (>90% of the National Television System Committee (NTSC)) [124]. However, the unsatisfactory emission band with 54 nm FWHM and emission peak position of 540 nm of the green-emitting β -SiAlON:Eu²⁺ phosphors makes difficult to achieve the superior white color gamut display. Thus, various narrow-band emitting green color phosphors were attempted to be built for many color display



Fig. 11. EL spectra and luminescence of pc-WLEDs devices obtained from (a) red emitting phosphors of CaAlSiN₃:Eu² combination with blue and green emitting CsKNa_{1.48}Li_{0.5}(SiO₄)₄: $0.02Eu^{2+}$ (y = 0.5) phosphor, and (b) white-LEDs fabricated from the combination of blue emitting BaMgAl₁₀O₁₇:Eu²⁺ phosemitting phor, red CaAlSiN₃:Eu²⁺ phosphor, and green-emitting CsKNa_{0.98}Li (SiO₄)₄:0.02Eu²⁺ (y = 1.0) coated by the *n*-UV LED chip ($\lambda_{ex} = 370$ nm) [38]. (Reproduced with permission from ref. 38, copyright 2019, American Chemical Society).

applications [8,125]. However, for the backlighting of displays, the pure quantum efficiency and the long decay time of the phosphors were not sufficient. To solve the problem of wide color gamut for LCD backlighting, novel green emitting phosphors with efficient narrow band emission, suitable peak position, short lifetime, and superior quantum efficiency should be produced.

Xia et al. [4,32,68,126] proposed an attractive technique whereby a mineral-inspired structure improves the host lattice of phosphors for white LEDs. Indeed, multiple narrow-band emitting phosphors, such as $RbNa_3(Li_3SiO_4)_4:Eu^{2+}$, $RbNa_2K(Li_3SiO_4)_4:Eu^{2+}$, and $RbLi(Li_3SiO_4)_2:Eu^{2+}$ phosphors, were developed by screening the phosphors compounds of the UCr₄C₄ type structure with highly condensed structure and rigid framework [8,34,36,94,127]. The patent WO 2018/029304A1 filed by OSRAM Opto Semiconductor includes these compounds [128, 129]. Among these phosphors, RbLi(Li_3SiO_4)_2:Eu^{2+} is considered as a next-generation narrow-band emitting green phosphor, but these type of phosphors still face many technical limitations, such as poor chemical stability along with low quantum efficiency.

Liao et al. [33] developed RbNa(Li_3SiO_4)₂: Eu^{2+} phosphors by adding a Na⁺ ion to replace a Li⁺ cation in RbLi(Li_3SiO_4)₂: Eu^{2+} host lattice, resulting in efficient improvement of the chemical stability by maintaining the same narrow band green color emission peaking at 523 nm with a little blue shift attributed to the effect of Stokes shift. The photoluminescence excitation and emission spectra of the synthesized RbNa(Li₃SiO₄)₂:8%Eu²⁺ lithosilicate phosphors and their comparison with the photoluminescence excitation and emission spectra of β -SiA-ION:Eu²⁺ oxynitride phosphors and RbLi(Li₃SiO₄)₂:8%Eu²⁺ lithosilicate phosphors are shown in Fig. 12a.

The photoluminescence excitation spectrum displays a suitable peak that fully matches the emission of the InGaN blue-emitting chip and its emission has an efficient narrow-band green color emission with a suitable peak at 523 nm with 41 nm FWHM. Accordingly, considering the suitable peak position of the narrow-band green emission along with the high thermal stability of the RbNa(Li₃SiO₄)₂:8%Eu²⁺ lithosilicate phosphors, this phosphor is a promising candidate for LCD backlighting. The combination of the green-emitting RbNa(Li₃SiO₄)₂:8%Eu²⁺ lithosilicate phosphors with the commercially available red-emitting KSF: Mn⁴⁺ phosphors and the 455 nm narrow-band InGaN blue-emitting chip was used to fabricated a white LED. Fig. 12b shows the electroluminescence spectrum of the fabricated white LED.

The optimized white LED device generates an efficient and bright white light with a high quantum efficiency of 111.08 Im W^{-1} under the



RbNa(Li₃SiO₄)₂:Eu²⁺ based LCD Screen

CommercialLCD Screen

Fig. 12. (a) The comparison of the PLE and PL spectra of RbNa(Li₃SiO₄)₂:Eu²⁺, RbLi(Li₃SiO₄)₂:Eu²⁺, and β-SiAlON:Eu²⁺ phosphors (the insets display digital images of unground RbNa(Li₃SiO₄)₂:Eu²⁺ phosphors under 365 nm UV - the size of the crucible was Ø11 × 20 in mm²), (b) CIE 1931 white-LED color coordinate, NTSC standard, and color space (short dotted line), Rec. (blue line), white-LED device (red line), (c) emission spectrum of the white LED system manufactured with the green phosphors of RbNa(Li₃SiO₄)₂:Eu²⁺ and red emitting KSF:Mn⁴⁺ coated on InGaN blue emitting chip ($\lambda_{em} = 455$ nm) under 20 mA current, (d) schematic illustration of the LCD prototype configuration based on the pc-LEDs technique, the backlight of the white-LEDs as manufactured and illuminated, (f) the backlight panel of the LCD, and (g) contrast of the display images of the LCD screen based on RbNa(Li₃SiO₄)₂:Eu²⁺ phosphors and the commercial LCD screen with the backlight of the blue emitting chips, the yellow Y₃Al₅O₁₂:Ce³⁺, and red emitting K₂SiF₆:Mn⁴⁺ phosphors [33]. (Reproduced with permission from ref. 33, copyright 2019, Wiley).

applied current of 20 mA with a superior wide color gamut of 113% NTSC. In addition, the produced light-emitting diodes show a wide color gamut of 84.5% Rec. 2020 gamut of colors, as shown in Fig. 12c. The device manifested CIE color coordinates as (0.3393, 0.3372) and a low CCT value up to 5196 K. Moreover, using the synthesized RbNa (Li₃SiO₄)₂:8%Eu²⁺ based on 33 white LEDs, a 20.5 inch LCD screen was successfully developed.

The configuration of the manufactured LCD prototype is illustrated in Fig. 12d, while digital images of the produced and lightened white LEDs are illustrated in Fig. 12e. Fig. 12f shows the backlight panel of the fabricated LCD screen. Furthermore, the prepared RbNa(Li₃SiO₄)₂:8% Eu²⁺ lithosilicate-based LCD screen was compared with the commercially available LCD screen prepared from the combination of YAG:Ce³⁺ with red-emitting KSF:Mn⁴⁺ and blue-emitting InGaN chip. The performance of both the manufactured LCD screens is shown in Fig. 2g, which indicates that the manufactured LCD screen based on RbNa (Li₃SiO₄)₂:Eu²⁺ lithosilicate phosphors shows better visual performance compared to the commercially available LCD screen based on phosphors converted LEDs.

3.3. Near infrared LED for medical diagnostics

The research on inorganic phosphors converted LEDs towards a wide-range of applications in the field of infrared light emission has opened up an important and intersecting coaduvant therapy pathway that leads to a reduction in the impact of cerebrovascular accidents and traumatic brain injuries. The growing knowledge of near-infrared lightemitting diodes offers the opportunity to increase the availability of cost-effective near-infrared LEDs for various medical diagnoses and treatments. More specifically, the technology of the near-infrared LEDs can be used to prepare an oxygen molecular examination, intervention therapy, and neuroimaging to provide the most reliable and successful aid in the diagnosis as well as in the treatment of the diseases. In addition, infrared light is used to accelerate the healing of tissue after an injury. There is much advancement in the near-infrared light-emitting technologies, for the generation of the most suitable wavelength. However, further work and materials capable of emitting near-infrared light are needed.

Benefiting from the development of the white light-emitting phosphors converted LEDs technology, the combination of near infraredemitting phosphors with the blue-emitting chip is an ideal candidate for the development of near-infrared LED. The near infrared-emitting phosphors have many advantages compared to the conventional tungsten and halogens lamp. The near-infrared light-emitting phosphors converted LEDs show high energy efficiency, excellent durability, and compact size, making them very promising candidates for various spectroscopic analysis and medical diagnoses. The transition metal Cr^{3+} activated phosphors display broad-band emission with a longer wavelength region attributed to Cr^{3+} occupation in the weak octahedral crystal structure [130–138].

Qiao et al. [139] developed near-infrared emitting rare-earth (Eu²⁺)

doped phosphors for the next-generation of infrared LEDs applications, such as photonics, optoelectronics, and biological applications. More interestingly they synthesized $K_3LuSi_2O_7:Eu^{2+}$ phosphors, which emit a wide-band emission centered at 740 nm with an FWHM of 160 nm. The structural and spectroscopic analysis shows that the unexpected near-infrared emission, which is a result of the occupation of the divalent Eu^{2+} ions in various LuO_6 and K_2O_6 polyhedra with small coordination numbers. The UCr₄C₄ type nitride compounds often have a symmetrical and highly rigid structural environment for occupying the divalent Eu^{2+} ions, resulting in longer wavelength emission.

It was P. Pust and coworkers [22] who synthesized various compounds of nitride phosphors with the UCr₄C₄ type structure. Various compounds of the produced nitride phosphors result in higher red emission wavelength ranging from 550 to 750 nm with the longest emission peak at 675 nm, as shown in Fig. 13a and b. The longer wavelength emission of compounds of the UCr₄C₄ type structure highlights the possibility of using various structural modifications to extend the emission wavelength to the near-infrared region. The addition of the trivalent Cr^{3+} , Pr^{3+} , and Yb^{2+} activators in UCr₄C₄ type phosphors compounds opens a new window for the generation of novel near-infrared phosphors for the development of near-infrared LEDs.

4. Challenges of UCr_4C_4 type narrow band phosphors - a promising strategy

4.1. Chemical stability

The development of highly efficient narrow-band green and redemitting luminescence materials is an urgent demand for their practical applications related to LCD backlighting with a wide color gamut [1,14,36]. Due to their specific luminescence characteristics and flexible chemical compositions, the narrow-band emitting phosphors with UCr₄C₄ type structure gained special interest [21,34,38,68,94]. The unusual luminescence characteristics along with the narrow-band emission of these materials due to their highly condensed and rigid framework structure and symmetric crystallographic sites occupying the activator leads to highly efficient narrow-band emission in blue, cyan, green, and red spectral regions with superior thermal stability [28,32, 35,140].

For instance, RbLi(Li₃SiO₄)₄:Eu²⁺ lithosilicate phosphors display a highly efficient narrow green band emission centered at 530 nm with 42 nm FWHM, which is comparable to the commercially available β -SiA-ION:Eu²⁺ green phosphors [36]. Nonetheless, the luminescence of these lithosilicate phosphors suffers due to the poor chemical stability in humid environments, which is probably a result of the low temperature of synthesis and the presence of alkali ions in the phosphors host lattice. The poor stability of lithosilicate phosphors restricts the use of these phosphors in practical commercial applications due to the degradation of light-emitting diodes after long term operation. Accordingly, the chemical stability of these narrow band emitting lithosilicate phosphors against moisture must be urgently improved.



Fig. 13. (a) Excitation, reflectance (dashed curves) and emission (λ_{ex} 440 nm) spectra measured at room temperature from bulk samples of M [Mg₂Al₂N₄]:0.1%Eu²⁺, where M = Ba, Sr, Ca, i.e. Ba [Mg₂Al₂N₄]:Eu²⁺ (blue line), Sr [Mg₂Al₂N₄]:Eu²⁺ (green curve), and Ca [Mg₂Al₂N₄]:Eu²⁺ (orange line), and (b) temperature dependence of photoluminescence spectra of M [Mg₂Al₂N₄]:0.1%Eu²⁺ nitride phosphors [22]. (Reproduced with permission from ref. 22, copyright 2014, American Chemical Society). In recent decades, remarkable advances have been made in exploring successful methods for solving the problem related to the exposure to humidity and the improvement of the chemical stability of the unstable luminescence materials, such as quantum dots (QDs). Typically, the coating method is used, such as the coating of hydrophobic organic layer or inorganic layer on the surface of materials.

4.2. Re-absorption phenomenon and low quantum efficiency

In order to correctly reflect a high-quality color in an accurate way, the source of illumination must provide photons with all wavelengths that are visible to our eye. A great challenge is the achievement of such a wide band emission from a single-phase phosphor. One or more light-emitting diodes coated with one or more phosphors yield a cumulative emission that appears white in commercially available white light sources. However, multiple emitters, due to the unequal degradation rates for the emitters and losses of efficiency due to reabsorption, result in variety of emission color over time due to the overlapping of the different components of absorption and emission energies [141–144]. Hence, it is important to build a novel device architecture that can efficiently reduce reabsorption in a white light-emitting device built from different color component phosphors. Furthermore, a single material that emits broadband white light with a continuous emission spectrum (400–700 nm) will also solve these problems [33,145–147].

4.3. High PLQYs near infrared emission

The near-infrared LEDs based on phosphors display fascinating nearinfrared emission allowing them to be widely used in plant lighting, biomedicine, infrared detectors, optical communications, and other fields. However, the overall performance of phosphor compounds with UCr₄C₄ type structure shows a narrow band emission under the excitation of blue light up to the red wavelength region and there is no satisfactory emission of UCr₄C₄ type compounds in the infrared and near-infrared region. This implies that the luminous efficacy, brightness, and stability of the UCr₄C₄ type phosphors must be further improved by (i) substitution of different cations and anions to tune the emission spectra to the near-infrared region, (ii) doping of different activators, such as Cr³⁺ and Pr³⁺ ions, to enhance energy formation, (iii) optimizing the preparation process for phosphors films, and (iv) carefully designing the LED system layout [148–150].

5. Conclusions

In modern LED lighting, backlight display, and information detection systems, traditional Eu²⁺ doped phosphors with UCr₄C₄ type structure are important luminescence materials for practical applications. In recent decades, considerable attention has been devoted to investigate the generation of narrow-band emission and its relation with the crystal structure. In this paper, we reviewed the luminescence tuning theory of the Eu^{2+} with chemical composition structure engineering and the recent developments in the UCr₄C₄ type structure narrow-band emitting phosphors. In order to demonstrate the possible applications in solidstate lighting, backlighting display, and near-infrared technologies, the developments of the narrow-band blue, cyan, green and red-emitting phosphors of the UCr₄C₄ type structure has been thoroughly investigated. In order to get a deep insight in these inorganic solid-state phosphors of the UCr₄C₄ type structure, we discussed the relationship between crystal structure and its modulations resulting in the enhancement of luminescence tuning ability. However, there are still many challenges and key issues in this field that have to be been extensively explored along with possible solutions.

Disclosures

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Declaration of competing interest

The Authors have no conflict of interest.

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